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ACCURACY AND REPEATABILITY INDICES  
FOR JOINT OIL ANALYSIS PROGRAM DATA

Douglas Carlton Hatcher



# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

ACCURACY AND REPEATABILITY INDICES  
FOR JOINT OIL ANALYSIS PROGRAM DATA

by

Douglas Carlton Hatcher

September 1979

Thesis Advisor:

D. R. Barr

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ACCURACY AND REPEATABILITY INDICES FOR JOINT OIL ANALYSIS  
PROGRAM DATA

by

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from the  
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September 1979



## ABSTRACT

This thesis examines spectrometric oil analysis data in an attempt to construct tables of statistical estimates for use in evaluating a laboratory's performance individually and in comparison to a control laboratory. Tables of estimates were obtained from data provided by twenty six laboratories.



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## I. INTRODUCTION

In 1956, the Naval Air Rework Facility at Pensacola started a trial program to determine if spectrometric analysis of oil samples could be used to predict aircraft engine failures. The Naval Oil Analysis Program (NOAP) evolved as a consequence of the success of the trial program. The program has been expanded to include monitoring virtually all Navy lubricated systems. In 1976, NOAP was merged with similar Army and Air Force programs and became the Joint Oil Analysis Program (JOAP). References 1 and 2 provide a more detailed background of the oil analysis program.

The prediction of a pending equipment failure is facilitated by the spectrometric oil analysis of a sample of the lubricating fluid from the equipment. The fluid sample is burned in the spectrometer and the concentrations of certain individual wearmetal elements in parts per million (PPM) are determined by the wavelengths of the light emitted. A record maintained for each equipment contains the results for each wearmetal concentration from previous samples. After a sample from a particular piece of equipment is burned, an evaluator reviews the results of current and past burns to determine if there is an abnormal trend development or abnormal concentration level. Depending on which wearmetals or combination of wearmetals have developed an abnormal trend, the evaluator is frequently able to pinpoint the source and recommend the required preventive maintenance action to the equipment custodian. Reference 3 contains procedures, intervals for sampling and normal limits of wearmetal concentrations for



some of the equipments monitored by JOAP.

The normal limits of wearmetal concentrations are not precise boundaries. One abnormal sample from a given equipment does not necessarily constitute a requirement for a maintenance action. Many factors must be considered by the evaluator. Typically a shorter sampling interval or an immediate resample may confirm an abnormal level or may lead the evaluator to conclude that some error has occurred (sample contamination or sample interchange). Other factors are the tolerances within which a laboratory can obtain the same results on repeated experiments (repeatability), and can reproduce either its own or another laboratory's results (reproducibility). These two factors are considered in this thesis.

Intuitively, it can be seen that a laboratory must be capable of obtaining fairly consistent results for repeated burns of an oil sample. Otherwise there would be little reason to expect the laboratory to provide data from which the evaluator would detect a discrepant equipment. We might expect also that the procedure would often identify a properly functioning equipment as being discrepant. Similarly, because military equipments are frequently transferred from one location to another, it is desirable to be able to use the results from different laboratories for the same equipment without having to wait for each laboratory to separately develop trend information about that equipment. As a means of insuring that consistent results are provided by laboratories, a certification program exists in JOAP (reference 3). The procedures for certification consider only an evaluation of a laboratory's individual performance. Reference 4 contains recommended procedures for laboratory certification involving both an evaluation of a laboratory's performance and its comparison with a control laboratory. Table 8-2 of reference 3



contains values of maximum allowable accuracy index and repeatability index for laboratory certification. But questions have arisen as to whether the values in the table refer to repeatability or reproducibility and what is the significance level of the values. Because of these questions there is some doubt about the validity of the numbers.

This thesis investigates data provided by twenty six laboratories that utilize the Baird Atomic AE35/U-3 Atomic Emission Spectrometer. The data collected are for 0, 3, 10, 50 and 100 PPM concentrations for each of twenty elements. Each sample analysis is replicated fifteen times and each set of fifteen replications is repeated on two different days.



## II. CONSIDERATIONS IN SPECTROMETRIC OIL ANALYSIS

### A. MEASUREMENT ERRORS

As discussed in reference 5, there are numerous potential sources of error in results from the atomic emissions spectrometer. For each observation taken (for each oil sample burned), the observed reading can be considered to include a true PPM reading plus an error term. The error term can be modeled as a random variable and, for the moment, can be thought of as an accumulation of the effects of all the possible sources of error. These sources include inputs such as temperature, humidity, electrode gap width, spectrometer standardization, inhomogeneous oil samples, operator technique, contamination, etc. The observed reading can be mathematically represented by:

$$Y_i = \mu + E_i \quad (1)$$

where  $Y_i$  is the result of the  $i^{\text{th}}$  observation,

$\mu$  is the true PPM, and

$E_i$  is the error component of the  $i^{\text{th}}$  observation.

Many of the error inputs can be controlled to some degree by careful attention to procedures established for the Oil Analysis Program. These include sample handling, spectrometer standardization and operator techniques.



However, in burning oil samples collected from operating equipments, the operator has no prior estimate of the true PPM of the sample nor of the error.

From equation (1), it can be seen that if the magnitude of the random error is allowed to be large relative to the true PPM, the error could mask a significant change in the estimated PPM. Since the error is not measurable, some method is needed to measure the performance of a spectrometer.

#### B. MEASURES OF PERFORMANCE

Since the random error term can be considered to be normally distributed (references 4, 5 and 6), good measures of spectrometer performance could be expected to involve functions of the sample mean and sample variance. To test whether a given spectrometer is producing results within an acceptable error tolerance level, one might make several observations on an oil sample of known PPM concentration and compute the sample mean and sample variance of the spectrometer readings. If the computed quantities were within some predetermined bounds, the spectrometer could be considered to be operating satisfactorily. Otherwise, the spectrometer should be realigned electronically (restandardized) and retested. The measures of performance currently used in JOAP are:

$$AI = |\mu - \bar{y}| \quad (2)$$

and

$$RI = \left( \sum_i (y_i - \bar{y})^2 / (N-1) \right)^{1/2}, \quad i = 1, \dots, N \quad (3)$$



where  $\mu$  is the known PPM concentration of the oil sample,

$$\bar{y} = \text{SUM}_i (y_i / N), \quad i = 1, \dots, N, \text{ is the sample mean,}$$

$y_i$  is the  $i^{\text{th}}$  observation on the sample,

$N$  is the total number of observations taken,

AI is the accuracy index (true PPM - sample mean), and

RI is the repeatability index (sample standard deviation).

For the reasons cited above, it was decided that the measures of performance represented by equations (2) and (3) are satisfactory for use with oil analysis program data.

Currently used values of the maximum allowable AI and RI are given in table 8-2 of reference 3. In their work with data obtained from the oil analysis program, D. R. Barr, T. Jayachandran, and H. J. Larson have found that the tabulated values may not be realistic bounds (reference 4).

As current doctrine in the JOAP procedure, an operator makes ten sample burns from a standard oil sample of known PPM concentration and uses equations (2) and (3) to compute AI and RI for each element under analysis. If the computed AI and RI do not exceed tabulated values, the laboratory is considered to be operating within acceptable tolerances. Otherwise, the operator should restandardize the spectrometer and repeat the sample burns.



### III. ANALYTICAL RESULTS

#### A. OBJECTIVES

The goal of this project was to statistically estimate the bounds or limits for AI and RI for both the within laboratory effect (repeatability) for a single laboratory, and between laboratory effect (reproducibility) for a given laboratory compared with a control laboratory. However, it was discovered that three separate and distinct sets of indicies could be identified. Appendix B is devoted to a development of the three sets of bounds for the indices. Notationally, the three situations are identified as Case I, Case II and Case III.

#### B. RESULTS

The procedures presented in this section apply to any one of the twenty elements for which the AE35/U-3 spectrometer is used in JOAP. They concern standardization with standard oil samples having any one of 0, 3, 10, 50 or 100 PPM concentrations. The procedures should be applied for each element and concentration of interest.

##### 1. Case I

Case I corresponds to the current usage of AI and



RI, that is, a laboratory makes a set of N sample burns with a standard oil sample and computes AI1 and RI1 using equations (2) and (3). The computed quantities (using n = 10 or n = 15 sample burns) may be compared with the bounds contained in table I or IV respectively of the next section. If the computed quantities are not greater than the tabled values, the laboratory's spectrometer may be considered to be operating within acceptable tolerances for Case I.

AI1 is the magnitude of the deviation of the sample mean from the known PPM concentration and might be viewed as an indicator of spectrometer alignment or standardization. RI1 is a measure of the variability in the spectrometer's observations. Excess variability suggests either poor operator technique or an erratic spectrometer channel.

## 2. Case II

Case II may be considered to be the tolerances within which a given laboratory would be expected to reproduce its own results with a second complete set of N sample burns from the same oil sample. The laboratory could complete these procedures using any oil sample. The following computations would be made for the two sets of sample burns:

$$AI2 = |\bar{y} - \bar{x}| \quad (4)$$

and

$$RI2 = \left( \frac{s_y}{s_x} \right)^2 \quad (5)$$

where  $\bar{y}$  is the sample mean computed from the first set of sample burns,



$\bar{x}$  is the sample mean computed from the second set of sample burns,

$s_y$  is RI1 computed from the first set of burns, and

$s_x$  is RI1 computed from the second set of burns.

The computed quantities (using  $N = 10$  or  $N = 15$  sample burns) from equations (4) and (5) may be compared with the bounds given in Table II or V respectively of the next section. If the computed value of AI2 from equation (4) is not greater than the tabled bound and if the computed value of RI2 from equation (5) lies between the reciprocal of the tabled value and the tabled value, the laboratory may be considered to be operating within acceptable tolerances for Case II.

AI2 is the magnitude of the deviation of sample means between sets of  $N$  observations and might be viewed as an indicator of a change in spectrometer standization. RI2 is a ratio of sample variances and measures a laboratory's ability to reproduce its previous results.

A word of caution concerning the interpretation of the index RI2 is in order. During the analyses, it was noted that the computed sample standard deviations from data sets taken from within a spectrometer appeared to be related. The correlation coefficient (appendix C) was computed for each PPM concentration and element combination and tested for significance (Table VII). Because the correlation noted was in general quite high, it should be expected that in almost all applications of Case II procedures, for RI2, the laboratory will pass.



### 3. Case III

Case III may be considered to be the tolerances within which a given laboratory would be expected to reproduce the results obtained by a control laboratory. Under Case III procedures, both the control laboratory and the laboratory under test would complete N sample burns on the same oil sample. The following computation would be made for the two sets of sample burns.

$$AI3 = |\bar{y} - \bar{x}| \quad (6)$$

and

$$RI3 = \left( \frac{s_y}{s_x} \right)^2 \quad (7)$$

where  $\bar{y}$  is the sample mean of the control laboratory's N observations,

$\bar{x}$  is the sample mean of the test laboratory's N observations,

$s_y$  is RI1 for the control laboratory, and

$s_x$  is RI1 for the test laboratory.

The computed quantities (using  $N = 10$  or  $N = 15$  sample burns) may be compared with the bounds given in table III or VI respectively of the next section. If the computed value of AI3 from equation (6) is not greater than the tabled bound and if the computed value of RI3 from equation (7) lies between the reciprocal of the tabled bound and the tabled bound, the laboratory under test may be considered to be operating within acceptable tolerances for Case III.



$A_{I3}$  is the magnitude of the deviation between a control laboratory's and a given laboratory's sample means and might be viewed as an indicator of a given laboratory's alignment with respect to the control laboratory.  $R_{I3}$  is a ratio of sample variances and measures a laboratory's ability to reproduce the control laboratory's results.

#### C. TABLES

Tables I through VII are discussed in section III and in appendices B and C. Table VIII is a comparison of the number of laboratories for which the data submitted was used with the number of laboratories submitting data (see discussion). Table IX is an example of the computer output for one of the 100 analysis of variance problems (100 PPM and element combinations). Appendices A, B and C have developments for most of table IX. Tables I through VII are taken from the 100 computer output pages. Table X is also taken from the computer output pages and shows for which PPM and element combinations the spectrometer effect was significant (appendix A).



TABLE I

## CASE I: AII AND RII FOR N = 10 SAMPLE BURNS

PPM	FE	AG	AL	BE	CR	CW	MG	NA	NI	PB	SI	SN	TI	B	BA	CD	MN	MO	V	ZN	
0	AI	0.6	0.6	0.8	0.7	0.8	0.6	0.7	1.4	0.7	1.5	0.5	1.4	1.0	0.8	0.7	1.2	0.9	1.3	2.3	0.7
	RI	0.5	0.2	0.8	0.3	0.8	0.4	0.5	1.3	0.8	1.4	0.6	1.3	0.7	0.6	0.5	2.5	0.4	1.6	2.2	1.0
3	AI	0.8	0.9	1.4	1.1	1.0	0.7	0.8	1.1	0.7	1.1	0.8	1.5	1.2	1.2	1.4	1.5	0.8	1.7	1.8	1.1
	RI	1.1	0.4	1.2	0.5	0.8	0.6	0.6	0.8	0.7	0.9	1.0	1.6	0.6	0.7	0.6	1.2	0.5	1.1	2.2	0.7
10	AI	1.2	1.3	2.0	2.2	1.8	1.4	1.5	1.7	1.2	1.2	0.5	2.4	1.8	1.9	1.6	2.0	1.5	2.2	2.5	3.0
	RI	1.2	0.7	1.7	0.9	1.0	0.7	1.0	2.3	0.8	1.1	1.1	2.0	1.3	1.1	0.9	2.5	0.7	1.8	2.8	1.1
50	AI	5.8	7.2	5.4	4.9	5.4	5.5	6.5	6.2	5.2	5.4	4.8	5.9	7.2	6.4	4.9	5.0	5.4	7.0	6.4	9.3
	RI	4.6	3.8	4.2	4.1	3.4	2.8	4.6	3.8	2.7	3.8	3.3	3.3	4.1	4.0	3.2	4.3	3.3	5.7	3.0	8.3
100	AI	8.0	13.2	9.5	8.2	10.5	8.8	13.5	17.6	10.2	10.8	7.4	9.8	10.8	13.1	8.3	12.5	9.2	12.0	8.7	18.9
	RI	8.3	11.7	9.1	7.4	4.4	6.1	8.5	9.3	5.0	6.2	5.4	5.2	10.6	9.6	6.5	10.7	6.7	9.8	4.8	19.9



TABLE II

## CASE II: AI2 AND RI2 FOR N = 10 SAMPLE BURNS

PPM	FE	AG	AL	BE	CR	CU	MG	NI	FB	SI	SN	T1	B	BA	CD	MN	MO	V	ZN	
0	AI	0.6	0.3	0.9	0.4	0.5	0.3	0.6	1.9	0.7	2.3	1.1	1.3	0.8	0.9	0.6	1.4	3.3	0.7	
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	
3	AI	1.0	1.0	1.9	1.1	1.0	0.9	0.6	1.1	0.9	1.6	1.0	3.0	1.5	1.8	0.9	1.9	0.9	2.2	2.3
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	
10	AI	1.2	1.2	1.9	2.0	1.5	1.1	1.3	2.1	1.4	1.5	1.2	2.6	2.1	2.5	1.9	1.8	1.3	2.5	2.9
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	
50	AI	6.1	8.5	6.4	7.0	7.5	7.6	6.2	7.1	5.7	5.6	6.0	5.0	7.7	8.7	6.0	7.5	7.4	7.9	5.9
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	
100	AI	12.2	16.9	9.0	11.2	12.8	12.6	22.7	17.1	11.1	13.6	11.2	10.4	13.5	14.4	8.6	17.2	11.6	16.4	11.9
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	



TABLE III

CASE III: A13 AND R13 FOR N = 10 SAMPLE BURNS

PPN	FE	AG	AL	BE	CR	CU	MG	NA	NJ	FB	SI	SN	TI	8	RA	CD	MN	MO	V	ZN	
0	AI	6.9	0.8	1.1	0.9	1.1	0.9	1.0	1.9	1.0	2.1	1.2	2.1	1.4	1.1	1.0	1.7	1.3	1.6	3.3	1.0
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
3	AI	1.1	1.3	2.0	1.5	1.4	1.1	1.1	1.5	1.0	1.5	1.2	2.7	1.7	1.8	2.0	2.2	1.2	2.4	2.6	1.6
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
10	AI	1.7	1.8	2.8	3.0	2.5	2.0	2.1	2.4	1.7	1.8	1.3	3.4	2.5	2.7	2.7	2.8	2.2	3.1	3.6	4.2
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
50	AI	6.2	10.1	7.7	6.9	7.6	7.8	9.1	8.7	7.4	7.7	6.8	8.4	10.1	9.1	7.0	7.0	7.7	9.9	9.0	13.2
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
100	AI	11.3	16.7	13.4	11.6	14.8	12.4	19.1	24.9	14.4	15.2	10.5	13.9	15.3	18.6	11.7	17.6	13.6	17.0	12.3	26.0
	RI	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0



TABLE IV

## CASE I: ALL AND RII FOR N = 15 SAMPLE BURNS

PPM	FE	AG	AL	BE	CR	GU	MG	NA	NI	PE	SI	SN	TI	B	BA	CD	MH	MD	V	ZN	
0	AI	0.6	0.6	0.8	0.7	0.8	0.6	0.7	1.3	0.7	1.4	0.8	1.4	1.0	0.8	0.7	1.1	0.9	1.2	2.3	0.7
	RI	0.5	0.2	0.7	0.3	0.8	0.4	0.5	1.2	0.7	1.3	0.8	1.2	0.6	0.6	0.4	2.2	0.3	1.5	2.0	1.0
3	AI	0.7	0.9	1.4	1.1	1.0	0.7	0.7	1.0	0.7	1.1	0.6	1.5	1.2	1.2	1.4	1.5	0.8	1.6	1.8	1.1
	RI	1.1	0.4	1.1	0.5	0.7	0.5	0.5	0.7	0.7	0.8	0.9	1.5	0.6	0.6	0.5	1.1	0.5	1.0	2.0	0.6
10	AI	1.2	1.3	2.0	2.1	1.7	1.4	1.4	1.7	1.2	1.2	0.9	2.4	1.7	1.5	1.6	2.0	1.5	2.2	2.5	3.0
	RI	1.1	0.6	1.5	0.8	1.0	0.7	0.9	2.1	0.8	1.1	1.1	1.8	1.2	1.0	0.8	2.3	0.7	1.7	2.5	1.0
50	AI	5.7	7.1	5.4	4.9	5.4	5.5	6.4	6.1	5.2	5.4	4.8	5.9	7.1	6.4	4.9	4.9	5.4	6.9	6.4	9.2
	RI	4.3	3.5	3.8	3.7	3.2	2.6	4.3	3.5	2.5	3.5	3.1	3.1	3.8	3.7	3.0	4.0	3.1	5.3	2.8	7.7
100	AI	7.8	13.0	9.4	8.1	10.4	8.7	13.4	17.5	10.1	10.7	7.3	9.7	16.6	13.6	8.2	12.3	9.1	11.9	8.6	18.5
	RI	7.7	10.9	8.3	6.9	4.1	5.7	8.0	8.8	4.7	5.8	5.1	4.9	9.8	9.0	6.1	9.9	6.2	9.2	4.5	18.5



TABLE V

## CASE III: AI2 AND RI2 FOR N = 15 SAMPLE BURNS

PPM	FE	AG	AL	BE	CR	CU	MG	NA	NI	FB	SI	SN	TI	θ	BA	CD	MN	MD	V	ZN	
0	AI	0.6	0.3	0.8	0.4	0.5	0.2	0.6	1.9	0.7	2.2	1.1	1.3	6.8	6.5	0.6	0.8	0.6	1.4	3.3	0.6
	RI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
3	AI	1.0	1.0	1.9	1.1	1.0	0.8	0.6	1.1	0.9	1.5	1.0	3.0	1.5	1.8	6.8	1.8	0.9	2.1	2.2	1.5
	RI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
10	AI	1.2	1.1	1.9	2.0	1.5	1.1	1.2	2.0	1.4	1.5	1.1	2.6	2.1	2.5	1.8	1.7	1.3	2.4	2.8	4.5
	RI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
50	AI	6.0	8.4	6.4	6.9	7.5	7.6	6.1	7.0	5.6	5.6	6.0	5.0	7.6	8.6	5.9	7.4	7.3	7.7	5.9	6.4
	RI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
100	AI	12.0	16.6	8.8	11.1	12.8	12.5	22.6	16.8	11.0	13.5	11.1	10.3	13.2	14.1	8.4	17.1	11.5	16.2	11.9	25.1
	RI	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0



TABLE VI

CASE III: A13 AND R13 FOR N = 15 SAMPLE BURNS

PBM	FE	AG	AL	BE	CR	CU	MG	NA	NI	PB	SI	SN	TI	B	BA	CD	MN	MD	V	ZN	
C	A1	0.9	0.8	1.1	0.9	1.1	0.9	1.0	1.0	2.0	1.2	2.0	1.4	1.1	1.0	1.6	1.3	1.7	3.3	1.0	
	R1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
3	A1	1.0	1.3	2.0	1.5	1.4	1.0	1.1	1.5	1.0	1.5	1.1	2.6	1.7	1.7	2.0	2.1	1.2	2.3	2.5	1.6
	R1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
10	A1	1.7	1.8	2.8	3.0	2.5	2.0	2.0	2.4	1.6	1.8	1.3	3.3	2.5	2.7	2.3	2.8	2.2	3.1	3.5	4.2
	R1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
50	A1	8.1	10.1	7.6	6.9	7.6	7.8	9.0	8.6	7.3	7.6	6.7	8.4	10.0	9.0	6.9	6.9	7.6	9.7	9.0	13.0
	R1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
100	A1	11.0	18.4	13.2	11.5	14.7	12.2	18.9	24.7	14.3	15.1	10.3	13.8	15.0	18.4	11.6	17.4	12.8	16.8	12.2	26.2
	R1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	



TABLE VII

## CORRELATION COEFFICIENT BETWEEN DAY I AND DAY II STANDARD DEVIATIONS

PPM	FE	AG	AL	BE	CR	CU	MG	NA	NI	PB	SI	SN	TI	B	BA	CD	MN	MD	V	ZN	
0 R	0.68	0.17	0.71	0.39	0.88	0.87	-0.15	0.40	0.53	0.19	0.21	0.12	0.39	0.26	0.45	0.29	-0.26	0.65	0.47	-0.06	
TAIL	0.0	0.41	0.0	0.08	0.0	0.0	0.0	0.47	0.07	0.01	0.38	0.31	0.61	0.05	0.26	0.04	0.19	0.26	0.0	0.03	0.81
3 R	0.29	0.23	0.77	0.69	0.34	0.48	0.39	0.07	0.60	0.73	0.39	0.12	0.44	0.66	0.71	0.52	0.66	0.54	0.43	0.31	
TAIL	0.16	0.25	0.0	0.0	0.09	0.01	0.05	0.78	0.00	0.0	0.05	0.64	0.02	0.00	0.0	0.01	0.00	0.01	0.06	0.20	
10 R	0.25	-0.05	0.87	0.57	0.60	0.28	0.69	0.82	0.16	0.63	0.35	0.37	0.55	0.18	0.25	0.28	0.35	0.57	0.85	0.25	
TAIL	0.09	0.80	0.0	0.00	0.00	0.17	0.0	0.0	0.45	0.00	0.08	0.10	0.00	0.41	0.25	0.21	0.11	0.00	0.0	0.34	
50 R	0.67	0.18	0.71	0.57	0.64	0.63	0.52	-0.11	0.29	0.40	0.55	0.33	0.39	0.33	0.41	0.36	-0.01	0.02	0.21	-0.25	
TAIL	0.0	0.38	0.0	0.01	0.0	0.0	0.01	0.63	0.15	0.65	0.00	0.12	0.05	0.15	0.05	0.11	0.95	0.91	0.39	0.39	
100 R	0.72	0.56	0.41	0.35	0.42	0.47	0.55	0.64	0.50	0.59	0.61	0.72	0.80	0.93	0.59	0.81	0.50	0.72	0.04	0.46	
TAIL	0.0	0.00	0.04	0.11	0.03	0.02	0.00	0.00	0.01	0.00	0.00	0.0	0.0	0.0	0.02	0.0	0.02	0.0	0.86	0.10	



TABLE VIII

## NO. OF LABS USED/NO. OF LABS SUBMITTED

PPM	0	3	10	50	100
FE	25/25	26/26	25/26	26/26	26/26
AG	25/25	26/26	26/26	26/26	26/26
AL	24/25	23/25	26/26	26/26	26/26
BE	21/21	22/22	22/22	21/22	21/22
CR	25/25	26/26	26/26	25/26	26/26
CU	25/25	26/26	26/26	26/26	26/26
MG	25/25	26/26	26/26	26/26	25/26
NA	22/22	20/23	21/23	21/23	19/23
NI	25/25	26/26	26/26	26/26	26/26
PB	24/24	25/25	25/25	24/25	23/25
SI	25/25	26/26	26/26	26/26	26/26
SN	21/23	19/24	21/23	23/25	23/24
TI	25/25	26/26	26/26	26/26	25/26
B	21/23	23/24	23/24	20/24	22/24
BA	22/23	24/24	23/24	23/24	23/24
CD	22/22	23/23	22/23	21/23	21/23
MN	21/22	21/21	22/24	21/23	21/23
MO	25/25	24/26	25/26	24/26	24/26
V	22/22	20/23	20/23	19/22	21/23
ZN	19/21	19/21	19/21	14/19	14/20



TABLE IX

PPM: 0 ELEMENT: FE

LAB	YIJ. BAR		STANDARD DEVIATION	
	DAY 1	DAY 2	DAY 1	DAY 2
1	-0.233	0.060	0.226	0.203
2	0.053	-0.067	0.368	0.232
3	0.093	0.007	0.194	0.428
4	-0.260	-0.547	0.210	0.270
5	-0.313	-0.620	0.181	0.227
6	-0.333	-0.047	0.238	0.136
7	-0.667	0.200	0.488	0.414
8	0.233	0.300	0.206	0.169
9	0.347	0.227	0.213	0.258
11	-0.300	-0.320	0.256	0.462
12	-0.000	0.153	0.314	0.484
13	0.480	0.773	0.457	0.433
14	-0.373	-0.407	0.128	0.139
15	0.120	-0.120	0.278	0.347
16	-0.540	-0.687	0.192	0.239
17	-0.067	-0.200	0.184	0.165
18	-0.500	0.240	0.125	0.083
19	0.0	0.0	0.0	0.0
20	-0.073	-0.053	0.313	0.242
21	0.0	0.0	0.0	0.0
22	-0.087	-0.140	0.300	0.282
23	0.013	0.013	0.164	0.270
24	-0.153	0.147	0.136	0.458
25	0.347	-0.247	0.449	0.400
26	-0.427	0.060	0.592	0.447

GRAND MEAN (Y... BAR) CORR COEF  
-0.092 0.680

## ANOVA TABLE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARES
MEAN	1.	6.366	
BETWEEN INSTRUM	24.	48.553	2.023
DAY WITHIN INST	25.	16.740	0.670
WITHIN INSTRUM	700.	60.971	0.087
TOTAL	750.	132.630	

  

SOURCE	F STATISTIC	F VALUE	COMP VAR EST
BETWEEN INSTRUM	3.0213	1.9643	0.045
DAY WITHIN INST	7.6875	1.5219	0.039
WITHIN INSTRUM			0.087

## TABLE VALUES FOR 10 BURNS

	CASE I	CASE II	CASE III
AI	0.615	0.631	0.869
RI	0.520	4.026	4.026

## TABLE VALUES FOR 15 BURNS

	CASE I	CASE II	CASE III
AI	0.606	0.615	0.857
RI	0.484	2.979	2.979



TABLE X

## SIGNIFICANT SPECTROMETER EFFECT

PPM	0	3	10	50	100
FE	YES	NO	YES	YES	NO
AG	YES	YES	YES	YES	NO
AL	YES	NO	YES	YES	YES
BE	YES	YES	YES	NO	NO
CR	YES	YES	YES	NO	NO
CU	YES	YES	YES	NO	NO
MG	YES	YES	YES	YES	NO
NA	NO	YES	NO	YES	YES
NI	YES	NO	NO	YES	YES
PB	NO	NO	NO	YES	NO
SI	NO	NO	NO	NO	NO
SN	YES	NO	YES	YES	YES
TI	YES	NO	NO	YES	NO
B	NO	NO	NO	NO	YES
EA	YES	YES	YES	NO	YES
CD	YES	NO	YES	NO	NO
MN	YES	YES	YES	NO	NO
MO	YES	NO	YES	YES	NO
V	NO	NO	YES	YES	NO
ZN	YES	NO	NO	YES	NO



#### IV. DISCUSSION AND CONCLUSIONS

The data submitted was, in general, assumed to be a representative sampling from the population of AE35/U-3 spectrometers used by JOAP. However, from  $\bar{x}$  vs s plots (reference 9) made from the sample means and sample standard deviations of the data, it appears that some laboratories submitted data which was not consistent with the data from other laboratories. Assistance, in determining which sets of data appeared to be erratic or from spectrometer channels with set up (standardization) problems, was obtained from the JOAP Technical Support Center. Table VIII shows the number of laboratories from which the data was used compared with the number of laboratories submitting data. In general, only those sets of data for which the laboratory appeared to stand apart from the rest on the  $\bar{x}$  vs s plot and were identified by the Technical Support Center were removed from the analyses. It is felt that a few of the laboratories may have been more than conscientious in setting up the spectrometer for the sample burns while a few others may have been somewhat careless. If this were indeed the situation, the variability (caused by the two extremes) could have been responsible for the apparent correlation noticed (table VII) for many PPM concentrations and element combinations. This would contribute erroneously to the sums of squares due to error, making the estimates larger in magnitude than they should be.

The tables of estimates are in a crude form: perhaps smoothing over elements and PPM concentrations could reduce



the coarseness of the values. To use the tables for PPM concentrations between those given, the user might use either linear interpolation or least squares regression. Linear least squares regression was tried using PPM as the independent variable and the estimate as the dependent variable. In general, a good fit was obtained. However, some of the tabled values appear to be outliers and in those cases the results were not usable. Using Bartlett's test for equal variances (appendix B), it was found that the assumption of equal (homogeneous) variances was not valid. According to Neter and Wasserman (reference 9), unequal variances can have pronounced effects on inferences about the variance components (appendix A) when using a random effects model.

Future work in this area should include a repeat of this project with a qualified observer present at each laboratory for the data gathering to ensure that proper standardization procedures are followed. In this project, it was found that the day (standardization) effect was significant for all PPM and element combinations. In many instances, the F statistic was more than ten times larger than the tabled F value (appendix A).

Because the day effect was significant in all cases, it is felt that the Case II procedures described in this report could be very useful to JOAP. Case I procedures (currently used in JOAP) used in conjunction with case II and case III procedures might ensure that laboratories could produce consistent results on both interlaboratory and intralaboratory comparisons.



## APPENDIX A

### MATHEMATICAL MODEL

An Analysis of Variance Model (references 7 and 9) is a statistical tool utilized by an experimenter to study the relationship between a dependent variable (an observation on a sample burn) and one or more independent variables (mean PPM concentration, spectrometers, standardization setting, error, etc). No assumptions are required about the nature of the statistical relation. The effects of the independent variables are separately studied by partitioning the total sum of squares (the summation of all the observations squared) and the associated degrees of freedom into smaller sums of squares that are specifically related to the independent variables. Dividing a sum of squares for an effect by its associated degrees of freedom gives an unbiased variance estimate (mean square). A ratio of two variance estimates, under the null hypothesis that the particular effect is zero, has an F distribution with degrees of freedom  $v_1$  (numerator degrees of freedom) and  $v_2$  (denominator degrees of freedom). At a chosen level of significance, the test statistic, F (the ratio of variance estimates), can be tested for significant effect by comparing F with the tabled value of an F distribution with  $v_1$  and  $v_2$  degrees of freedom. A value of F greater than or equal to the tabled value (at the chosen level of significance) implies that the effect is significant; otherwise, it may be considered to be zero. Analysis of



Variance models may be used for fixed effects (levels of independent variables under study are the only ones of interest) or for random effects (levels of independent variables under study are a subset of a population that is of interest).

The model used in analyses of the data is a Nested Random Effects Model (reference 7). A random effects model is considered appropriate because it allows for generalization of the results obtained from the randomly selected subset of a population (spectrometers) of interest to the entire population. Twenty five laboratories were chosen from the population of 127. The laboratories were selected by drawing uniform random numbers between 1 and 127 until twenty five laboratories had been selected. However, those laboratories based aboard ships and in foreign countries were exempted from selection. The time required to mail oil samples to the exempted laboratories and for them to return the results was thought to be excessive.

In the random selection of oil laboratories for participation in the data collection, the laboratory expected to be the control laboratory (JOAP Technical Support Center) was not selected. However, it was considered desirable to have the control laboratory included in the sampling. Hence, data were also collected from Technical Support Center, making twenty six laboratories in total. The addition of the non-randomly selected laboratory to the sample should not significantly alter the generalization of the results to the entire population of spectrometers. The nested feature of the model allowed the author to investigate the day (standardization) effect within spectrometers.

The model can be expressed mathematically as:



$$Y_{ijk} = \mu + A_i + B_{j(i)} + E_{ijk},$$

$i = 1, \dots, I$ ,  $j = 1, \dots, J$ ,  $k = 1, \dots, K$

where  $Y_{ijk}$  is the  $k^{\text{th}}$  observation from the  $i^{\text{th}}$  spectrometer

on day  $j$ ,

$\mu$  is the mean effect,

$A_i$  is the  $i^{\text{th}}$  laboratory effect,

$B_{j(i)}$  is the  $j^{\text{th}}$  day effect within laboratory  $i$ , and

$E_{ijk}$  is the random error of the  $k^{\text{th}}$  observation on instrument  $i$  and day  $j$ .

The assumptions of the model are that  $E_{ijk}$  is

distributed  $NI(0, \sigma_A^2)$ ,  $A_i$  is distributed  $NI(0, \sigma_A^2)$ , and  $B_{j(i)}$

is distributed  $NI(0, \sigma_B^2)$  for each  $i$ . The notation  $NI(0, \sigma^2)$

means normally and independently distributed with mean 0 and

variance  $\sigma^2$ .

The assumption of a normal distribution for observations on oil sample burns seems reasonable and is documented by previous work with oil analysis data (references 4, 5 and 6). The assumption of independence is somewhat questionable based on previous work. It has been found that there exists a dependence between certain elements and a dependence between PPM concentrations (references 4, 5 and 6). However, in view of the fact that all of the analyses in



this report were performed for one PPM concentration and one element at a time, the assumption of independence does not seem unreasonable.

The sums of squares for the model (reference 7) are:

$$SSM = IJK(\bar{Y}_{...})^2,$$

$$SSA = JK * \text{SUM}_i (\bar{Y}_{i...} - \bar{Y}_{...})^2 = \text{SUM}_i (\bar{Y}_{i...})^2 / JK - SSM,$$

$$SS(B|A) = K * \text{SUM}_{i,j} (\bar{Y}_{ij.} - \bar{Y}_{i...})^2$$

$$= \text{SUM}_{i,j} (\bar{Y}_{ij.})^2 / K - \text{SUM}_i (\bar{Y}_{i...})^2 / JK,$$

$$SSE = \text{SUM}_{i,j,k} (\bar{Y}_{ijk} - \bar{Y}_{ij.})^2$$

$$= \text{SUM}_{i,j,k} (\bar{Y}_{ijk})^2 - \text{SUM}_{i,j} (\bar{Y}_{ij.})^2 / K,$$

$$SSTO = \text{SUM}_{i,j,k} \bar{Y}_{ijk}$$

$$i = 1, \dots, I, j = 1, \dots, J, k = 1, \dots, K \quad (a1)$$

where  $SSM$  is the sum of squares due to the mean effect,

$SSA$  is the sum of squares due to the laboratory effect,

$SS(B|A)$  is the sum of squares due to the day within spectrometer effect,

$SSE$  is the sum of squares due to the random error



effect,

SSTO is the total sum of squares,

$$\bar{Y}_{...} = \text{SUM}_{i,j,k} Y_{ijk} / IJK, \quad \bar{Y}_{i..} = \text{SUM}_{j,k} Y_{ijk} / JK ,$$

$$\bar{Y}_{ij.} = \text{SUM}_k Y_{ijk} / K , \quad i, j \text{ and } k \text{ are defined in equation (a1),}$$

I is the number of laboratories, J is the number of days sampled, and K is the number of replications for each laboratory and day combination.

The mean squares for the model (reference 7) are:

$$MSA = SSA / (I-1) ,$$

$$MS(B|A) = SS(B|A) / I(J-1) , \text{ and}$$

$$MSE = SSE / IJ(I-1) \quad (a2)$$

where MSA is the mean squares due to the spectrometer effect,

MS(B|A) is the mean squares due to the day (standardization) within spectrometer effect, and

MSE is the mean squares due to random error.

The two test statistics associated with the model are:

$F_A = MSA / MS(B|A)$  with  $(I-1)$  and  $I(J-1)$  degrees of freedom and

$F_B = MS(B|A) / MSE$  with  $I(J-1)$  and  $IJ(K-1)$  degrees of



freedom,

(a3)

where  $F_A$  is the test statistic used to test for a significant spectrometer effect and

$F_B$  is the test statistic used to test for a significant day effect.

The usual estimators for the components of variance are:

$$\hat{\sigma}_A^2 = \text{MSE},$$

$$\hat{\sigma}_B^2 = (\text{MS}(B|A) - \text{MSE})/K, \text{ and}$$

$$\hat{\sigma}_A^2 = (\text{MSA} - \text{MS}(B|A))/JK. \quad (a4)$$



## APPENDIX B

### ESTIMATORS FOR AI AND RI

While developing bounds on AI for the three cases, it was found that for variance estimates the usual chi-square statistic was not appropriate. The sum of  $k$  independent chi-square distributed random variates  $(n_i^2 S_i^2 / \sigma_i^2)$  with  $n_i$  degrees of freedom (reference 8) is a chi-square random variate  $(n^2 S^2 / \sigma^2)$  with  $n = n_1 + n_2 + \dots + n_k$  degrees of freedom. However, the variance estimates used in determining the bounds for AI were linear combinations of variances for which Cochran's theorem is not applicable. Using the procedures described in chapter 17 of reference 8, an approximate chi-square statistic can be formed as follows:

$$u = ng/G \quad (b1)$$

where  $n = (\sum_{i=1}^k g_i x_i)^2 / \sum_{i=1}^k (g_i x_i^2 / n_i)$ ,  $i = 1, \dots, K$ , is the approximate degrees of freedom,

$$G = g_1 \sigma_A^2 + g_2 \sigma_B^2 + g_3 \sigma_C^2,$$



$$g = g_1 MSA + g_2 MS(B|A) + g_3 MSE,$$

$x_1 = MSA$ ,  $x_2 = MS(B|A)$ ,  $x_3 = MSE$  and the  $g_i$ 's will be defined in the development that follows for the variance estimates.

#### A. CASE I

A 95 percent confidence bound on  $AI1 (\mu - \bar{Y}_{ij})$ , is

given by  $t_n (.975) g^{1/2}$ ,

where  $\bar{Y}_{ij}$  is the sample mean of K observations with the ith spectrometer on day j,

g is a variance estimate of  $(\mu - Y_{ij})$

n is the approximate degrees of freedom, and

$t_n (.975)$  is the tabled value of Student's t distribution having n degrees of freedom.

The variance of  $(\mu - Y_{ij})$  can be found as follows:

$$V(\mu - Y_{ij}) = V(Y_{ij}) = V(\sum_k Y_{ijk}/K)$$

$$= (1/K^2) V(\sum_k (\mu + A_i + B_j + E_{ijk}))$$



$$= 1/K \left( K \sigma_A^2 + K \sigma_B^2 + \sum_k V(E_{ijk}) \right)$$

$$= \sigma_A^2 + \sigma_B^2 + \sigma^2 / 15, \quad k = 1, \dots, K$$

An estimate,  $g$ , of  $V(\mu - Y_{ij.})$  is (from equation (a4)):

$$g = g_1 MSA + g_2 MS(B|A) + g_3 MSE,$$

$$g_1 = 1/JK, \quad g_2 = (J-1)/JK \text{ and } g_3 = (K-N)/KN, \quad (b2)$$

where I is the number of spectrometers used in the analysis,

J is the number of days (2),

K is the number of repeated observations, and

N is the number of sample burns for which tables were constructed (10 or 15).

The approximate degrees of freedom n associated with the variance estimate g is:

$$n = [g_1 MSA + g_2 MS(B|A) + g_3 MSE] / \\ [g_1^2 (MSA)^2 / (I-1) + g_2^2 (MS(B|A))^2 / I(J-1) + g_3^2 (MSE)^2 / IJ(K-1)] \quad (b3)$$

The usual 95 percent upper confidence bound on RI1 would be  $[n(MSE) / \chi_n^2 (.05)]^{1/2}$ , where n is the degrees of freedom associated with the variance estimate, MSE, and  $\chi_n^2 (.05)$  is



the tabled value of a chi-square distribution having n degrees of freedom. During analysis it was found that this upper bound on RI<sub>1</sub> was not realistic when compared with the sample standard deviations computed from the data. A Bartlett test for equal variances was performed (reference 9) for several PPM and element combinations. It was found that for all combinations tested, the hypothesis of equal variances was rejected. Therefore, another method for estimating the upper bound on RI<sub>1</sub> was developed.

To estimate the upper bound on RI<sub>1</sub>, the sample standard deviations for both days on all spectrometers were used to construct an empirical cumulative distribution function. The 95 percent upper bound was found by linear interpolation on the empirical cumulative distribution function.

To find the upper bound on RI<sub>1</sub> for N = 10 sample burns, it is assumed that the upper tail of the distribution of sample variances can be approximated by the upper tail of a normal distribution. To develop a relation between the distributions for 10 and 15 sample burns, it is further assumed that the sample variances have first and second moments that are related in the same manner as those of chi-square variates. The variance of a chi-square variate

$(v_i s_i^2 / \sigma_i^2)^2$  is  $2v_i$  (reference 7), and

$$V(S_1^2) = \sigma^4 / v_1^2 V(v_1 s_1^2 / \sigma_1^2)^2 = 2 \sigma^4 / v_1$$

and, from the 95 percent upper bound we have

$$P(S_1^2 \leq R I_1^2) = .95$$

$$\text{or, } P((S_1^2 - \sigma^2) / (2 \sigma^4 / v_1)^{1/2} \leq (R I_1^2 - \sigma^2) / (2 \sigma^4 / v_1)^{1/2}) = .95$$



$$\text{or, } \Phi\left(\frac{(RI_1 - \sigma^2)}{\sqrt{2\sigma^2/v_1}}\right) = .95$$

where  $s_1^2$  is the estimate of sample variance for  $N = 15$

sample burns,

$v_1$  is the degrees of freedom of the estimate ( $v_1 = 14$ ),

and

$\Phi$  is the standard normal CDF.

After equating the above to a similar statement for  $N = 10$  sample burns, we have:

$$RI_{10} = ((14/9)^{1/2} RI_{15}^2 - (1 - (14/9)^{1/2}) \sigma^2)^{1/2}$$

Replacing  $\sigma^2$  by its estimate (MSE) gives the upper bound on  $RI_{10}$  for  $N = 10$  sample burns.

## B. CASE II

A 95 percent confidence bound on  $AI_2 (|\bar{y} - \bar{x}|)$  is given by  $t_n(.975) g^{1/2}$ , where  $\bar{y}$  is the sample mean of the first set of  $N$  observations, and  $\bar{x}$  is the sample mean of the second set of  $N$  observations.

The variance of  $(Y_{ij} - Y_{ij'})$  can be found as follows:



$$V(\bar{Y}_{ij\cdot} - \bar{Y}_{ij'\cdot}) = V(\bar{Y}_{ij\cdot}) + V(\bar{Y}_{ij'\cdot}) - 2\text{Cov}(\bar{Y}_{ij\cdot}, \bar{Y}_{ij'\cdot})$$

$$\text{Cov}(\bar{Y}_{ij\cdot}, \bar{Y}_{ij'\cdot}) = E(\bar{Y}_{ij\cdot} - \mu)(\bar{Y}_{ij'\cdot} - \mu) = \sigma_A^2,$$

$$\text{Hence, } V(\bar{Y}_{ij\cdot} - \bar{Y}_{ij'\cdot}) = 2\sigma_B^2 + 2\sigma_A^2/15.$$

An estimate,  $g$ , of  $V(\bar{Y}_{ij\cdot} - \bar{Y}_{ij'\cdot})$  is (from equation (a4)):

$$g = g_1 MSA + g_2 MS(B|A) + g_3 MSE$$

$$g_1 = 0, g_2 = 2/K, \text{ and } g_3 = 2(K-N)/KN \quad (b4)$$

The approximate degrees of freedom,  $n_i$ , are found using equation (b3) with the  $g_i$ 's as defined in equation (b4).

A 95 percent confidence interval on  $RI2 \left( \frac{s_y^2}{s_x^2} \right)$  is given by:

$$1/F_{n^1, n^2}(.975) \leq RI2 \leq F_{n^1, n^2}(.975) \quad (b5)$$

where  $F_{n^1, n^2}(.975)$  is the tabled value of an F distribution having  $n^1$  and  $n^2$  degrees of freedom.

Since the number of observations,  $N$ , is the same for both sets of observations  $n^1 = n^2 = N-1 = 9$  or 14.



C. CASE III

A 95 percent bound on  $A13 (|\bar{y} - \bar{x}|)$  is given by

$$\frac{t_n(0.975)}{\sqrt{n}} g^*,$$

where  $\bar{y}$  is the sample mean of the control laboratory's N observations, and

$\bar{x}$  is the sample mean of the given laboratory's N observations.

The variance of  $(\bar{Y}_{ij.} - \bar{Y}_{i'j'})$  is found as follows:

$$V(\bar{Y}_{ij.} - \bar{Y}_{i'j'})$$

$$= V(\bar{Y}_{ij.}) + V(\bar{Y}_{i'j'}) - 2Cov(\bar{Y}_{ij.}, \bar{Y}_{i'j'})$$

$$Cov(\bar{Y}_{ij.}, \bar{Y}_{i'j'}) = 0$$

$$V(\bar{Y}_{ij.} - \bar{Y}_{i'j'}) = 2 \sigma_A^2 + 2 \sigma_B^2 + 2 \sigma^2 / 15$$

An estimate,  $g$ , of  $V(\bar{Y}_{ij.} - \bar{Y}_{i'j'})$  is (from equation (a4)):

$$g = g_1 MSA + g_2 MS(B|A) + g_3 MSE,$$



$$g_1 = 2/JK, \quad g_2 = 2(J-1)/JK, \quad \text{and} \quad g_3 = 2(K-N)/KN \quad (b6)$$

The appropriate degrees of freedom,  $n$ , are found using equation (b3) with the  $g_i$ 's as defined in equation (b6).

The 95 percent bound on RI3 is found using equation (b5).



## APPENDIX C

### CORRELATION

During analysis of the data provided by the participating laboratories, the sample standard deviations were computed and the correlation coefficient (reference 9) was computed as follows:

$$r_{num} = \sum_{i=1}^I x_i y_i - \sum_{i=1}^I x_i \sum_{i=1}^I y_i / N$$

$$r_{denom} = ((\sum_{i=1}^I x_i^2 - (\sum_{i=1}^I x_i)^2 / N) (\sum_{i=1}^I y_i^2 - (\sum_{i=1}^I y_i)^2 / N))^{1/2}$$

$$r = r_{num}/r_{denom}, i = 1, \dots, I \quad (c1)$$

where  $y_i$  is the sample standard deviation computed from the data collected on the first day that data was collected for each PPM and element combination,

$x_i$  is the sample standard deviation computed from the data collected on the second day, and

I is the number of laboratories submitting data for a given PPM concentration.

Table VII gives the values of the correlation coefficient r for each PPM and element combination. To determine whether the correlation coefficients computed were



significant, the test statistic t was computed as follows:

$$t = r(I - 2)^{1/2} / (1 - r^2)^{1/2} \quad (5)$$

Under the hypothesis that the correlation is zero, t is distributed as Student's t distribution with I - 2 degrees of freedom (reference 9). Entering a t distribution table with the test statistic t and I - 2 degrees of freedom yielded the tail areas that are also given in Table VII. If one chose .05 as the desired level of significance, any tail area listed in Table VII not greater than .05 would imply that the corresponding correlation coefficient is significant: there is a significant positive correlation between the standard deviations of the first and second day's observations at a given laboratory. The discussion above assumes that the day one and day two sample standard deviations are observations on a bivariate normal population (reference 9). However, sample standard deviations are not normally distributed. Hence, the results in table VII should only be interpreted as rough indicators.



## APPENDIX D

### PARTICIPATING LABORATORIES

the following is a list of the laboratories that cooperated by making the sample burns and submitting their results for the author's analyses. The numbering system has no relation to the oil analyses program.

Lab no.      Location of laboratory

- 1      Technical Support Center, Pensacola
- 2      McClellan AFB
- 3      Hunter AAF
- 4      NAS Norfolk
- 5      MCAS Cherry Point
- 6      Langley AFB
- 7      Pease AFB
- 8      Laughlin AFB
- 9      Bergstrom AFB
- 10     NAS Whidbey Island
- 11     Dover AFB
- 12     FT Rucker
- 13     Dyess AFB
- 14     Myrtle Beach AFB
- 15     ANG, Jacksonville, Fl
- 16     Davis Monthan AFB
- 17     McChord AFB
- 18     Shaw AFB
- 19     Eglin AFB
- 20     Holloman AFB
- 21     Randolph AFB
- 22     Minot AFB



23           NAS Alameda  
24           Ft Hood  
25           Grandfork AFB  
26           Ellsworth AFB



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